However, one can conclude that the planarity of the molecule of 3,6 -diphenyl-s-tetrazine or $p$-terphenyl is the result of the intermolecular interactions rather than the result of the $\pi$-electron energy of the isolated molecule.

Thanks are due to Dr Yu . T. Struchkov for his kind assistance.

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# The Crystal Structure of $\mathrm{C}_{10} \mathrm{H}_{14} \mathrm{~N}_{4} \mathrm{O}_{2}$, a Heterocyclic Cage Compound 

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(Received 9 April 1971)


#### Abstract

A heterocyclic cage $\left(\mathrm{C}_{10} \mathrm{H}_{14} \mathrm{~N}_{4} \mathrm{O}_{2}\right)$ was recently synthesized from ethylenediamine and glyoxal. Through crystal-structure analysis, the molecule was shown to be a rigid cage containing five-, six-, and sevenmembered saturated heterocyclic rings. The compound crystallizes in space group $C 2 / c$ with $a=$ $11 \cdot 271 \pm 0.007, b=5.983 \pm 0 \cdot 004, c=14 \cdot 755 \pm 0.009 \AA$, and $\beta=106 \cdot 1 \pm 0 \cdot 1^{\circ}$. The asymmetric unit is a half-molecule ( $Z=4$ ), and the calculated crystal density is $1.545 \mathrm{~g} . \mathrm{cm}^{-3}$. X-ray intensity data were collected with an automatic diffractometer and refined to $R=0.053$. The structure was solved by the symbolic addition procedure for direct phase determination.


## Introduction

A new reaction between ethylenediamine (I) and glyoxal (II) was recently reported by Edwards, Weiss, Gilardi \& Karle (1968). A dilute aqueous solution of (I) and (II), in the molar ratio $2: 3$, reacted at room temperature to form a cage compound (III), $\mathrm{C}_{10} \mathrm{H}_{14} \mathrm{~N}_{4} \mathrm{O}_{2}$. Several distinct structural formulae are compatible with the chemical properties, nuclear magnetic resonance spectrum, and mass spectrum of this substance. Two possibilities are shown below:


Structure (III $a$ ) is composed entirely of six-membered heterocyclic rings, while (III $b$ ) contains five-, six-, and
seven-membered rings. Nevertheless, the environment of bonded neighbors about any chosen atom of (IIIa) is identical to the bonded environment of a corresponding atom of (IIIb), e.g., the N atoms are adjacent to one secondary and two tertiary carbon atoms in (IIIa) or (III $b$ ). The analysis of the X-ray diffraction data from a crystal of this substance unambiguously indicated (IIIb) to be the correct structure. Crystals of this substance were obtained from Drs J. M. Edwards and U. Weiss of the National Institute for Arthritis and Metabolic Diseases.

## Experimental

Crystals were grown from ethanol. The examination of the X-ray diffraction pattern of these apparently single crystals revealed that they were multiple. The material was extremely soluble in water, and it was found that single crystals could be quickly grown from a few drops of water on a microscope slide. The sharp diffraction pattern obtained from these crystals was identical in its spacings with the diffuse patterns obtained from the crystals grown from ethanol. A meltingpoint determination indicated no difference between the original and the recrystallized material.

Precession and Weissenberg diffraction photographs indicated that the crystal is monoclinic, with systematic absences characteristic of either of the space groups $C 2 / c$ or $C c$. Cell dimensions were obtained by aligning
the crystal on a diffractometer and measuring the pos－ itive and negative scattering angles（ $2 \theta$ values）of nine general reflections．Cell constants and other physical characteristics of the crystal are listed in Table 1.

Table 1．Physical data

| Habit | Colorless prisms |
| :---: | :---: |
| Crystal size | $0.25 \times 0.35 \times 0.45 \mathrm{~mm}$ |
| Space group | C2／c |
| $a$ | $11.271 \pm 0.007 \AA$ |
| $b$ | $5.983 \pm 0.004$ |
| c | $14.755 \pm 0.010$ |
| $\beta$ | $106 \cdot 1 \pm 0 \cdot 1^{\circ}$ |
| Volume | $956 \AA^{\text { }}$ |
| Density（calc） | $1 \cdot 545 \mathrm{~g} . \mathrm{cm}^{-3}$ |
| Radiation | $\mathrm{Cu} K \alpha(1.54178 \AA)$ |
| $\mu$ ，absorption coefficient | $9.37 \mathrm{~cm}^{-1}$ |
| Molecules per cell | 4 |
| $\langle \| E\rangle$ | $0 \cdot 803$ |
| $\langle \| E^{2}-1\| \rangle$ | 1.005 |

Intensity data were collected on a four－circle auto－ matic diffractometer using a conventional moving－crys－ tal moving－counter $(\theta-2 \theta)$ scan，with background counts at each end of the scan．All independent reflections out to a $2 \theta$ limit of $133^{\circ}$ were measured，leading to a set of 840 data．The data were corrected for Lorentz and polarization factors and placed on an absolute scale by means of a $K$ curve．Structure－factor magnitudes， $|E|$ ，were computed．The statistical averages，$\langle | E\rangle$ and $\langle | E^{2}-1| \rangle$（Table 1），strongly indicated a centric di－
stribution of $|E|$ values（Karle \＆Hauptman，1956）； thus，phase determination was begun assuming the space group to be $C 2 / c$ ．

## Structure determination and refinement

The symbolic addition procedure（Karle \＆Karle，1966） was used to determine the structure．In space group $C 2 / c$ ，only two phases need be assigned to specify the origin（Hauptman \＆Karle，1959）．Using this as a starting point，routine application of the procedure led to an $E$ map which containing structure（III $b$ ），cen－ tered on the crystallographic twofold axis at $x=\frac{1}{2}$ ， $Z=\frac{1}{4}$ ．

Isotropic and anisotropic refinement of the $\mathrm{C}, \mathrm{N}$ ， and O atoms led to an $R$ of $0 \cdot 128$ ，which decreased to $0 \cdot 10$ by addition of all the hydrogen atoms from a dif－ ference map．An examination of the largest discrep－ ancies indicated that the relatively high $R$ value was due to rather severe secondary extinction effects．Re－ moval of only four strong reflections from the refine－ ment lowered $R$ to $0 \cdot 075$ ．A statistical examination of the average discrepancy，$\langle | F_{v}\left|-\left|F_{c}\right|\right\rangle$ ，versus $\left|F_{v}\right|$ ，in－ dicated that the discrepancies were systematically and increasingly negative for values of $\left|F_{0}\right|>40$ ．Since only 48 reflections（approximately $6 \%$ of the data）were greater than this，it was feasible to eliminate this block of reflections from the refinement．Åsbrink \＆Werner （1966）eliminated approximately $10 \%$ of the reflections from a data set exhibiting severe secondary extinction

Table 2．Observed and calculated structure factors for $\mathrm{C}_{10} \mathrm{H}_{14} \mathrm{~N}_{4} \mathrm{O}_{2}$
Columns are index $l,\left|F_{0}\right| \times 10$ ，and $F_{c} \times 10$ ．Asterisks indicate reflections omitted from final refinement（see text）．


Table 3. Fractional coordinates and thermal parameters
The thermal expression is of the form:

$$
\begin{gathered}
T=\exp \left[-\frac{1}{4}\left(B_{11} h^{2} a^{* 2}+B_{22} k^{2} b^{* 2}+B_{33} l^{2} c^{* 2}+2 B_{12} h k a^{*} b^{*}+2 B_{13} h l a^{*} c^{*}+2 B_{23} k l b^{*} c^{*}\right)\right] . \\
\text { Nonhydrogen atoms }
\end{gathered}
$$

|  | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 0 | 48680 (10) | 62746 (22) | 16107 (9) | 2.41 (6) | 2.76 (6) | $4 \cdot 17$ (7) | $0 \cdot 30$ (4) | 1.05 (5) | $1 \cdot 19$ (4) |
| $\mathrm{N}(1)$ | 36640 (13) | 28911 (25) | 15637 (10) | $2 \cdot 12$ (6) | $2 \cdot 88$ (7) | $2 \cdot 92$ (7) | -0.05 (4) | 0.56 (5) | -0.23 (5) |
| N(2) | 61009 (13) | 28897 (24) | 18802 (11) | $2 \cdot 25$ (7) | $2 \cdot 85$ (7) | $3 \cdot 17$ (7) | 0.23 (4) | $1 \cdot 10$ (5) | -0.11 (5) |
| C(1) | 42756 (14) | 16284 (28) | 24073 (12) | $2 \cdot 21$ (8) | $2 \cdot 11$ (7) | $3 \cdot 53$ (8) | -0.37 (5) | $0 \cdot 84$ (6) | -0.03 (5) |
| C(2) | 38290 (15) | 52334 (29) | 18244 (13) | 1.98 (7) | 2.59 (8) | 3.87 (9) | 0.25 (5) | $0 \cdot 80$ (5) | $0 \cdot 42$ (6) |
| C(3) | 60165 (15) | 52382 (29) | 21092 (13) | 2.06 (7) | $2 \cdot 62$ (8) | 3.87 (9) | -0.07 (5) | 1.06 (6) | $0 \cdot 36$ (6) |
| C(4) | 40375 (18) | 22260 (41) | 7322 (14) | $3 \cdot 15$ (9) | $5 \cdot 34$ (11) | $3 \cdot 18$ (9) | -0.19 (7) | 0.69 (6) | -1.06 (7) |
| C(5) | 54654 (18) | 22221 (42) | 9207 (15) | $3 \cdot 31$ (9) | 5.07 (11) | $3 \cdot 50$ (9) | $0 \cdot 39$ (7) | 1.37 (7) | -0.85 (8) |

Table 3 (cont.)
Hydrogen atoms
Positional parameters are multiplied by 104 .

|  | $x$ | $y$ | $z$ |
| :---: | :---: | :---: | :---: |
| H(1) | 3674 (28) | 684 (57) | 539 (22) |
| H(2) | 3653 (28) | 3424 (59) | 173 (22) |
| H(3) | 3920 (23) | 148 (48) | 2378 (18) |
| H(4) | 3169 (26) | 6216 (45) | 1458 (20) |
| H(5) | 3359 (27) | 6226 (45) | 3093 (21) |
| H(6) | 4254 (28) | 879 (58) | 4176 (22) |
| H(7) | 4378 (28) | 3218 (56) | 4551 (24) |

(The hydrogen atoms were assigned thermal parameters equal to those of the adjoining heavier atom.)
and showed that this treatment compared favorably with various explicit correction schemes. Refinement of the abbreviated data set led to an $R$ of 0.053 for this compound; recalculation of the $R$ value for the full data set (including the reflections with secondary extinction errors) gave a value of 0.098 . All of the $R$ values quoted above are based on calculations which include the 'unobserved' (zero intensity) reflections. The observed and final calculated structure factors are listed in Table 2.

Full-matrix least-squares methods were used at all stages of the refinement; the function minimized was $\sum w\left(F_{o}-F_{c}\right)^{2}$. Each reflection intensity was initially given a weight of unity, and this was not changed until all hydrogen atoms were found. At this later stage, a statistical examination of the remaining discrepancies suggested the weighting function: $1 / w=1 \cdot 0+\left[\left(\left|F_{o}\right|-\right.\right.$ $4)[8]^{2}$, which gives a distribution of weights consistent with the distribution of errors expected in counter diffractometry. The positions of the hydrogen atoms were varied during the weighted refinement, and all converged satisfactorily. Each hydrogen atom was assigned a thermal parameter equal to that found for its neighboring heavier atom in the previous refinement cycle. The refined atomic parameters are given in Table 3.

## Discussion of structure

The cage structure (Fig. 1) can be viewed as two layers of boat-shaped six-membered rings. The lower layer
consists of two fused piperazine rings; the upper layer is a dioxane ring. The 'sides' of this cage are five-membered rings [Fig. $1(b)$ ] in the envelope conformation, and the ends are seven-membered rings which could also be described as boat-shaped.

The carbon-carbon bond which forms the junction of the piperazine rings $\left[C(1)-C\left(1^{\prime}\right)\right]$ is the only bond which appears to be significantly lengthened by cage formation (Fig. 2); its length is $1.574 \pm 0.003 \AA$ rather than the expected $1.53-1.55 \AA$ value. There are two pairs of eclipsed bonds interacting across this particular $\mathrm{C}-\mathrm{C}$ bond. This amount of lengthening is not unusual; a similar formation of eclipsed bonds about a C-C bond was observed, for example, by Schwarzenbach (1968) in the structure of a cage compound. The bond length reported there was also $1.574 \pm 0.008 \AA$.

(a)

(b)

Fig. 1. Two views of the cage skeleton: (a) projected down the crystallographic twofold axis, and (b) rotated $90^{\circ}$ from the first view about the long axis of the molecule.

The dioxane ring is restricted to the boat shape by the presence of nonbonded near neighbors, $\mathrm{C}(4)$ and C(5), within the same molecule. Each of these carbon atoms is only $2.78 \AA$ from the oxygen atom, whereas a $\mathrm{C} \cdots \mathrm{O}$ van der Waals approach would be greater than
$3.1 \AA$. The oxygen atoms are displaced $0.62 \AA$ from the plane of the four carbon atoms of the dioxane ring. The melting point $\left(300^{\circ} \mathrm{C}\right.$, Edwards et al., 1968) and the density ( $1.545 \mathrm{~g} . \mathrm{cm}^{-3}$ ) are rather high for crystals of an organic compound of this size, and suggest


Fig. 2. Bond distances and angles for $\mathrm{C}_{10} \mathrm{H}_{14} \mathrm{~N}_{4} \mathrm{O}_{2}$. E.s.d.'s, from the least-squares refinement, are $0 \cdot 0025-0.0035 \AA$ for bond distances and $0 \cdot 15-0.20^{\circ}$ for the bond_angles.


Fig. 3. The contents of one unit cell viewed in projection down the $b$ axis. Portions of molecules closest to the viewer are emphasized in black.
unusually tight packing. The packing is illustrated in Fig. 3. There are no opportunities for hydrogen bonding and no overall dipolar attractions. There are only a few intermolecular distances less than $3 \cdot 6 \AA$ (Fig. 3). However, each atom interacts with several atoms from neighboring molecules at distances only slightly longer ( 3.6 to $3.8 \AA$ ). The molecules mesh together neatly, accounting for the relatively high density.

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# The Crystal Structure of Ammonium Oxalate Monoperhydrate 

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(Received 21 May 1971 and in revised form 2 August 1971)


#### Abstract

The crystal structure of ammonium oxalate monoperhydrate $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{C}_{2} \mathrm{O}_{4} . \mathrm{H}_{2} \mathrm{O}_{2}$, has been determined from three-dimensional X-ray diffractometer data. The compound crystallizes in the orthorhombic space group $P 2_{1} 2_{1} 2$, with two molecules per unit cell. $6 \%$ of the $\mathrm{H}_{2} \mathrm{O}_{2}$ molecules are found to be exchanged with $\mathrm{H}_{2} \mathrm{O}$ molecules occupying randomly distributed sites. Both the oxalate ion and the hydrogen peroxide molecule are situated on twofold axes. The interatomic dimensions of the oxalate ion are normal, but the ion is non-planar. The planes of the two $\mathrm{C}-\mathrm{C}-\mathrm{O}_{2}$-groups of the ion are inclined at an angle of $28 \cdot 15(9)^{\circ}$. The hydrogen peroxide molecule has a skew conformation with a dihedral angle of 121 (3) $)^{\circ}$, the acceptor angle being $127.77(9)^{\circ}$. The interatomic dimensions are of normal values. All available hydrogen atoms are engaged in hydrogen bonds; $\mathrm{O}-\mathrm{H} \cdots \mathrm{O}$ is 2.625 (1) $\AA$ and the $\mathrm{N}-\mathrm{H} \cdots \mathrm{O}$ average distance is $2 \cdot 860$ (1) $\AA$. Single crystals of the perhydrate transform to single crystals of the hydrate over a period of several months. No variation in unit-cell dimensions is found for different batches of crystals, and no gradual variation in unit-cell dimensions seems to accompany the transformation from the perhydrate to the hydrate.


## Introduction

Investigations are being carried out at this institute to study the structure and bonding of the hydrogen peroxide molecule in solids (Pedersen, 1969a). Previously it has been found that the hydrogen peroxide molecule forms stoichiometric compounds with all the alkali metal oxalates. The crystal structures of the following compounds have been determined: $\mathrm{Li}_{2} \mathrm{C}_{2} \mathrm{O}_{4} \cdot \mathrm{H}_{2} \mathrm{O}_{2}$ (Pedersen, 1969b), $\mathrm{Na}_{2} \mathrm{C}_{2} \mathrm{O}_{4} \cdot \mathrm{H}_{2} \mathrm{O}_{2}$ (Pedersen \& Pedersen, 1964) $\mathrm{K}_{2} \mathrm{C}_{2} \mathrm{O}_{4} \cdot \mathrm{H}_{2} \mathrm{O}_{2}$ and $\mathrm{Rb}_{2} \mathrm{C}_{2} \mathrm{O}_{4} \cdot \mathrm{H}_{2} \mathrm{O}_{2}$ (Pedersen, 1967). Evidence has been found that caesium oxalate also forms a perhydrate. In this paper the crystal structure of ammonium oxalate monoperhydrate will be described in detail. A preliminary note (Pedersen, 1969c) has been published, but as indications of non-stoichiometry were found in this compound, a detailed discussion was postponed until more accurate intensity data were available.

The crystal structure of ammonium oxalate monoperhydrate is closely related to the structure of ammonium oxalate monohydrate (Robertson, 1965). A similar analogy has been observed previously for the potassium and rubidium oxalates, which also form
both monohydrates and monoperhydrates (Pedersen, 1967). The crystal structure of ammonium oxalate monohydrate, which has previously been carefully refined from three-dimensional X-ray data at $30^{\circ} \mathrm{K}$ (Robertson, 1965), shows all available hydrogen atoms to be engaged in hydrogen bonds and the oxalate ion to be non-planar, the dihedral angle between the two $\mathrm{C}-\mathrm{C}-\mathrm{O}_{2}$ planes being 26.6 (4) ${ }^{\circ}$. The non-planarity is believed to be caused by the hydrogen bonding network.
By substituting the water molecule by a molecule of hydrogen peroxide, one would expect changes in the crystal structure. Slight changes in packing and hydrogen bonding possibilities may lead to changes in the unusual twisted conformation of the oxalate ion, which hitherto has been observed only for the hydrogen oxalate ion (Haas, 1964; Pedersen, 1968; Follner, 1970; Tellgren \& Olovsson, 1971).
The hydrogen peroxide molecule in the gas phase has a dihedral angle of $111 \cdot 5^{\circ}$. The molecule has, however, been found to show great variation in dihedral angle, from 90 to $180^{\circ}$, in the solids that so far have been studied in detail. As ammonium oxalate contains only light atoms, it was hoped that the dimensions deter-

